4072 *Organometallics* **2005,** *24,* 4072−4078

Syntheses, Structures, and VT NMR Studies of Diselenophosphates of Group 14 Organometals. DFT Calculations for Gas-Phase Stability of Dinuclear Ions, $[(Ph_3M)_2\{\mu\text{-Se, Se-P(OR)}_2\}]^+$(M = Ge, Sn, and Pb)

C. W. Liu,[*,†] Tarlok S. Lobana,[‡,∥] Jie-Liang Xiao,[‡] Hong-Yuan Liu,[‡]
Ben-Jie Liaw,[‡] Chiu-Ming Hung,[‡] and Zhenyang Lin[*,§]

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan,
Department of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan, and
Department of Chemistry, Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Received April 16, 2005

Equimolar reactions of group 14 compounds, $(C_6H_5)_3MCl$ with $(NH_4)[Se_2P(OR)_2]$, in diethyl ether yielded the first organometallic derivatives of diselenophosphates, viz., $[Ph_3M\{\eta^1\text{-Se}(Se)P(OR)_2\}]$ [M= Ge, R = Et, ^{i}Pr, ^{n}Pr (**1−3**); Sn, Et, ^{i}Pr, ^{n}Pr (**4−6**); Pb, Et, ^{i}Pr, ^{n}Pr (**7−9**)]. The crystal structures of **1**, **4**, **6**, and **7** showed that the geometry around a metal center for each compound is distorted tetrahedral. The (η^1-Se) coordination mode with one pendant Se atom exhibited in these complexes is the new connective pattern for the diselenophosphates. ^{31}P and ^{77}Se NMR spectral studies reveal that whereas germanium compounds do not show lability of Ge−Se bonds, the Sn and Pb compounds do exhibit lability of Sn−Se and Pb−Se bonds, which involve exchange of the coordinated and pendant Se atoms at room temperature. This exchange process is slowed at low temperature and stopped at around 210 K. The exchange energy ($\Delta G^{\ddagger}$) is calculated to be in the range of 38−46 kJ mol^{-1} for compounds **4−9**. Positive FAB-mass spectral data reveal that germanium compounds **1** and **3** have nearly equal abundance of molecular ions $[(Ph_3M)\{\mu\text{-Se, Se-P(OR)}_2\}]^+$ and dinuclear cations $[(Ph_3M)_2\{\mu\text{- Se, Se-P(OR)}_2\}]^+$; the same is not true for tin and lead compounds **4**, **5**, **7**, and **8**, whose dinuclear cations are several times intense over their molecular ions. The structures of these dinuclear cations as well as their formation pathway have been studied by the density functional theory calculations.

Introduction

Diselenophosphates [dsep, $Se_2P(OR)_2^-$] have been known since 1968, but their coordination chemistry remained ignored, probably because of their oxidation and extrusion of Se from the ligand.[1−9] In the past decade Liu et al. have demonstrated the novelty of diselenophosphates by studying their coordination chemistry, particularly with elements from groups 11−13, and by preparing several unusual clusters and polynuclear compounds.[10−23] There are only two structurally characterized compounds among elements other than groups 11−13, namely, $[Mo_3(\mu_3\text{-Se})(\mu_2\text{-Se}_2)_3\{Se_2P(OEt)_2\}_3](Br)$[5] and $Ni[Se_2P(OEt)_2]_2$.[7] In sharp contrast, many

---

[*] To whom correspondence should be addressed. Fax: (+886)-3-8633570. E-mail: chenwei@mail.ndhu.edu.tw.

[†] National Dong Hwa University.

[‡] Chung Yuan Christian University.

[§] Hong Kong University of Science and Technology.

[∥] On leave from Guru Nanak Dev University, Amritsar 143005, India (tarlokslobana@yahoo.co.in).

(1) Kudchadker, M. V.; Zingaro, R. A.; Irgolic, K. J. *Can. J. Chem.* **1968**, *46*, 1415.

(2) Krishnan, V.; Zingaro, R. A. *Inorg. Chem.* **1969**, *8*, 2337.

(3) Baratova, Z. R.; Solozhenkin, P. M.; Semenov, E. V.; Mel'nik, Ya. I.; Grishina, O. N. *Dok. Akad. Nauk. Tadz. SSR* **1979**, *22*, 478 (Russian).

(4) Tomlinson, A. A. G. *J. Chem. Soc. A* **1971**, 1409.

(5) Bereau, V.; Ibers, J. A. *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 123.

(6) Krishnan, V.; Zingaro, R. A. *J. Coord. Chem.* **1971**, *1*, 1.

(7) Leemput, P. J. H. A. M.; Hummelink, Th. W.; Noordik, J. H.; Beurskens, P. J. *Cryst. Struct. Commun.* **1975**, *4*, 167.

(8) Das, R.; Prabhananda, B. S. *J. Magn. Reson.* **1983**, *54*, 89.

(9) Larin, G. M.; Dyatkina, E. *Izv. Akad. Nauk SSR, Ser. Khim.* **1972**, *6*, 1413.

(10) Liu, C. W.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C. *Chem. Commun.* **1998** 1831.

(11) Liu, C. W.; Shang, I.-J.; Wang, J.-C.; Keng, T.-C. *Chem. Commun.* **1999**, 995.

(12) Liu, C. W.; Hung, C.-M.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C.; Guo, K.-M. *Chem. Commun.* **2000**, 1897.

(13) Liu, C. W.; Chen, H.-C.; Wang, J.-C.; Keng, T.-C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2342.

(14) Liu, C. W.; Shang, I.-J.; Hung, C.-M.; Wang, J.-C.; Keng, T.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 1974.

(15) Liu, C. W.; Hung, C.-M.; Wang, J.-C.; Keng, T.-C. *J. Chem. Soc., Dalton Trans.* **2002**, 3482.

(16) Liu, C. W.; Hung, C.-M.; Santra, B. K.; Chen, H.-C.; Hsueh, H.-H.; *Inorg. Chem.* **2003**, *42*, 3216.

(17) Liu, C. W.; Hung, C.-M.; Santra, B. K.; Wang, J.-C.; Kao, H.-M.; Lin. Z. *Inorg. Chem.* **2003**, *42*, 8551.

(18) Santra, B. K.; Liaw, B.-J.; Hung, C.-M.; Liu, C. W. *Inorg. Chem.* **2003**, *42*, 8866.

(19) Liu, C. W.; Hung, C.-M.; Haia, H.-C.; Liaw, B.-J.; Liou, L.-S.; Tsai, Y.-F.; Wang, J.-C. *Chem. Commun.* **2003**, 976.

(20) Liu, C. W.; Haia, H.-C.; Hung, C.-M.; Santra, B. K.; Liaw, B.-J.; Lin, Z.; Wang, J.-C. *Inorg. Chem.* **2004**, *43*, 4464.

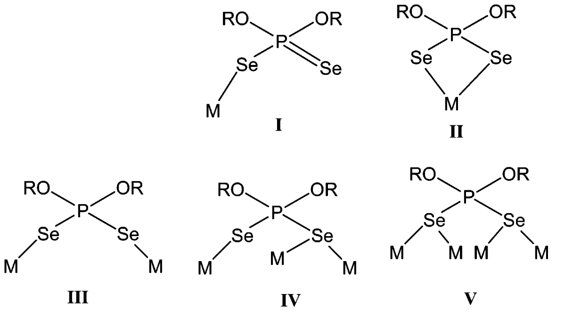
(21) Liu, C. W.; Hung, C.-M.; Santra, B. K.; Chu, Y.-H.; Lin, Z. *Inorg. Chem.* **2004**, *43*, 4306.

(22) Santra, B. K.; Hung, C.-M.; Liaw, B.-J.; Wang, J.-C.; Liu, C. W. *Inorg. Chem.* **2004**, *43*, 7570.

(23) Chen, J.-M.;Santra, B. K.; Liu, C. W. *Inorg. Chem. Commun.* **2004**, *7*, 1103.

10.1021/om050291q CCC: $30.25

Chart 1



studies on compositions and structures of complexes of analogous phosphor-1,1-dithiolate ligands have been reported.[24−34]

Four coordination modes of diselenophosphates have been identified in their metal complexes (II−V, Chart 1),[1−23] and mode I is being reported for the first time in this paper. In view of our interest to develop coordination chemistry of diselenophosphates as ligands and also after finding very interesting polynuclear complexes with Cu^I, Ag^I, and Zn^{II},[10−22] we were curious to look into main group elements. In this respect, indium(III) formed octahedral, tris-chelated complexes, $In[Se_2P(OR)_2]_3$, which in solution state showed lability of the In−Se bonds,[23] and in order to explore the generality of this observation, we were interested in investigating the interaction of dsep ligands with group 14 metals. Tin(II) and lead(II) were known to form $M[Se_2P(OEt)_2]_2$ (M = Sn, Pb),[2] but the synthesis and structural chemistry of tin(IV) and lead(IV) are unexplored. In this paper, the synthesis, multinuclear NMR spectroscopy, positive FAB mass, and crystal structures (**1**, **4**, **6**, and **7**) of diselenophosphate derivatives of organogermanium(IV), tin(IV), and lead(IV) are reported. The chemistry of related dithiophosphates with organogermanium(IV), tin(IV), and lead (IV) has been reported.[35−44] The solution-state fluxionality of tin and lead complexes as well as gas-phase stability of dinuclear ions, such as $[(Ph_3M)_2\{\mu\text{-Se, Se-P(OR)}_2\}]^+$ (M = Ge, Sn, Pb) are the interesting features of the studies. The exchange of free energy between coordinated and pendant Se donor atoms is also calculated for the tin and lead compounds. DFT calculations for dinuclear cations and molecular complexes are also carried out.

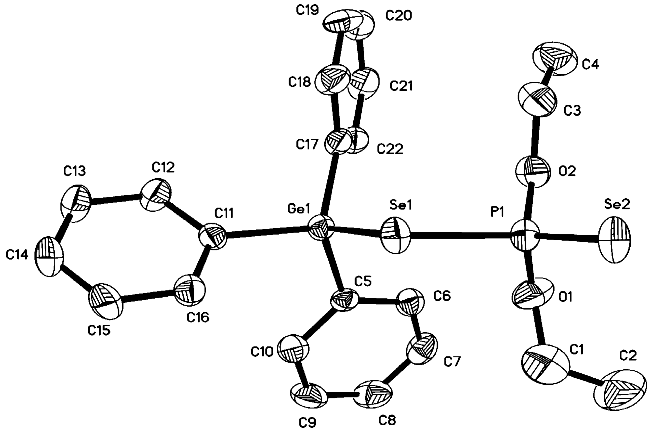


Figure 1. Thermal ellipsoid drawing (30% probability) of $[(C_6H_5)_3Ge\{\eta^1\text{-Se (Se)P(OEt)}_2\}]$, **1**, with atomic numbering scheme.

Results and Discussion

Synthesis. Equation 1 depicts the formation of compounds **1**−**9**, obtained by a metathetical reaction of Ph_3MCl (M = Ge, Sn, Pb) with a dsep ligand.

$$Ph_3MCl + (NH_4)[Se_2P(OR)_2] \xrightarrow[Et_2O]{N_2,\ 0\ ^\circ C} Ph_3M[Se(Se)P(OR)_2] + NH_4Cl \quad (1)$$

$$M = Ge,\ R = Et\ (\mathbf{1}),\ {}^iPr\ (\mathbf{2}),\ {}^nPr\ (\mathbf{3})$$

$$Sn,\ R = Et\ (\mathbf{4}),\ {}^iPr\ (\mathbf{5}),\ {}^nPr\ (\mathbf{6})$$

$$Pb,\ R = Et\ (\mathbf{7}),\ {}^iPr\ (\mathbf{8}),\ {}^nPr\ (\mathbf{9})$$

The yields were around 80−90%; compounds of Sn and Pb are stable to air and moisture, but those of Ge involve reaction with oxygen to form $Ph_3Ge\text{-O-}GePh_3$[45] and $(RO)_2P(Se)\text{-Se-Se-}P(Se)(OR)_2$. They are soluble in common solvents such as CH_2Cl_2, $CHCl_3$, acetone, etc. The compounds were characterized by their elemental analysis, FAB-mass, and X-ray crystallography for **1**, **4**, **6** and **7**. The solution-state behavior of all complexes was studied by using multinuclear NMR (^1H, ^{31}P, ^{77}Se) spectroscopy.

X-ray Structures. The crystal structures of compounds **1**, **4**, **6**, and **7** confirm the stoichiometry of all of the complexes as $[Ph_3M\{\eta^1\text{-Se(Se)P(OR)}_2\}]$ (M = Ge, Sn, Pb), and they are isostructural. The atomic numbering scheme for compound **1** is shown in Figure 1. In

---

(24) Haiduc, I.; Edelmann, F. T. *Supramolecular Organometallic Chemistry*; Wiley: Weinheim, New York, 1999.

(25) (a) Haiduc, I.; Sowerby, D. B.; Lu, S.-F. *Polyhedron* **1995**, *14*, 3389. (b) Haiduc, I. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amstredam, 2003; Vol. 1, pp 349−376.

(26) Haiduc, I.; Sowerby, D. B. *Polyhedron* 1995, *14*, 2469 and references therein.

(27) Wasson, R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch. (Top. Curr. Chem.)* **1973**, *35*, 65.

(28) Mehrotra, R. C.; Srivastava, G.; Chauhan, B. P. S. *Coord. Chem. Rev.* **1984**, *55*, 207.

(29) Molloy, K. C.; Zuckerman, J. J. *Acc. Chem. Res.* **1983**, *16*, 386.

(30) Tiekink, E. R. T. *Main Group Met. Chem.* **1992**, *15*, 161

(31) Haiduc, I. *Rev. Inorg. Chem.* **1981**, *3*, 353.

(32) Liu, C. W.; Stubs, R. T.; Staples, R. J.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1995**, *117*, 9778.

(33) Liu, C. W.; Pitts, J. T.; Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 3899.

(34) Fackler, J. P. Jr.; Staples, R. J.; Liu, C. W.; Stubs, R. T.; Lopez, C.; Pitts, J. T. *Pure Appl. Chem.* **1998**, *70*, 839.

(35) Rao, R. J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *53*, 203.

(36) Clark, H. C.; Jain, V. K.; Mehrotra, R. C.; Singh, B. P.; Srivastava, G.; Birchall, T. *J. Organomet. Chem.* **1985**, *279*, 385.

(37) Rao, R. J.; Srivastava, G.; Mehrotra, R. C. *J. Organomet. Chem.* **1983**, *258*, 155.

(38) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 1662.

(39) Singh, B. P.; Srivastava, G.; Mehrotra, R. C. *J. Organomet. Chem.* **1979**, *171*, 35.

(40) Begley, M. G.; Gaffney, C.; Harrison, P. G.; Steel, A. *J. Organomet. Chem.* **1985**, *289*, 281.

(41) Haiduc, I.; Martinas, F.; Ruse, D.; Curtui, M. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, *5*, 103.

(42) Chadha, R. K.; Drake, J. E.; Sarkar, A. B. *Inorg. Chem.* **1985**, *24*, 3156.

(43) Molloy, K. C.; Hossain, M. B.; van der Helm, D. Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1979**, *18*, 3507.

(44) Preut, H.; Ngo, V. D.; Huber, F. *Acta Crystallogr.* **1987**, *C43*, 164.

(45) (a) Glidewell, C.; Liles, D. C. *Acta Crystallogr. Sect B: Struct. Sci.* **1978**, *34*, 119.(b) Kuzmina, L, G. Struchkov, Yu. T. *J. Struct. Chem.* **1972**, *13*, 946.

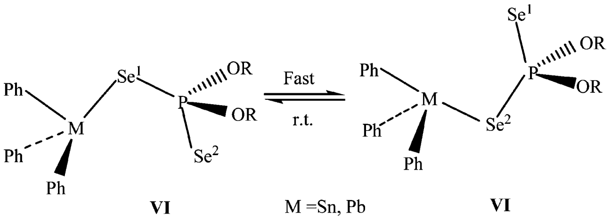
Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 4, 6, and 7

	1		
Ge(1)−C(17)	1.933(6)	Ge(1)−Se(1)	2.4050(9)
Ge(1)−C(5)	1.943(6)	Se(1)−P(1)	2.2190(17)
Ge(1)−C(11)	1.947(6)	Se(2)−P(1)	2.0775(17)
C(5)−Ge(1)−C(11)	110.3(2)	C(17)−Ge(1)−Se(1)	109.95(18)
C(17)−Ge(1)−C(11)	112.0(2)	C(5)−Ge(1)−Se(1)	112.19(16)
C(17)−Ge(1)−C(5)	112.4(2)	C(11)−Ge(1)−Se(1)	99.31(16)
Ge(1)−Se(1)−P(1)	105.24(5)	Se(1)−P(1)−Se(2)	109.63(8)
	4		
Sn(1)−C(13)	2.127(5)	Sn(1)−Se(1)	2.5705(8)
Sn(1)−C(1)	2.133(5)	Se(1)−P(1)	2.1940(16)
Sn(1)−C(7)	2.135(5)	Se(2)−P(1)	2.0764(16)
C(13)−Sn(1)−C(7)	112.18(19)	C(13)−Sn(1)−Se(1)	109.28(14)
C(1)−Sn(1)−C(7)	110.57(18)	C(1)−Sn(1)−Se(1)	113.99(13)
C(13)−Sn(1)−C(1)	110.40(19)	C(7)−Sn(1)−Se(1)	100.09(13)
Sn(1)−Se(1)−P(1)	101.52(4)	Se(1)−P(1)−Se(2)	112.68(7)
	6		
Sn(1)−C(13)	2.126(6)	Sn(1)−Se(1)	2.5734(8)
Sn(1)−C(7)	2.130(6)	Se(1)−P(1)	2.1855(19)
Sn(1)−C(1)	2.134(6)	Se(2)−P(1)	2.0759(18)
C(13)−Sn(1)−C(7)	110.0(2)	C(7)−Sn(1)−Se(1)	100.38(15)
C(1)−Sn(1)−Se(1)	109.53(15)	C(7)−Sn(1)−C(1)	111.9(2)
C(13)−Sn(1)−C(1)	110.5(2)	C(13)−Sn(1)−Se(1)	114.20(14)
Sn(1)−Se(1)−P(1)	101.05(5)	Se(1)−P(1)−Se(2)	112.82(8)
	7		
Pb(1)−C(5)	2.181(10)	Pb(1)−Se(1)	2.6577(12)
Pb(1)−C(11)	2.185(9)	Se(1)−P(1)	2.199(3)
Pb(1)−C(17)	2.206(9)	Se(2)−P(1)	2.071(3)
C(5)−Pb(1)−C(11)	108.5(3)	C(5)−Pb(1)−Se(1)	111.6(3)
C(5)−Pb(1)−C(17)	113.6(4)	C(11)−Pb(1)−Se(1)	98.7(2)
C(11)−Pb(1)−C(17)	114.9(3)	C(17)−Pb(1)−Se(1)	108.5(3)
Pb(1)−Se(1)−P(1)	101.77(8)	Se(1)−P(1)−Se(2)	111.05(13)

compound **1**, the Ge atom is bonded to three carbon atoms of three phenyl groups with approximately equal Ge−C bond distances (1.933, 1.943, and 1.947 Å), and to one Se atom of $[(EtO)_2PSe_2]^-$ with Ge−Se(1) bond distance of 2.405(1) Å. These Ge−C and Ge−Se bond distances are close to the sum of the covalent radii of Ge, C (1.99 Å), and Ge, Se (2.44 Å), respectively.[46] The coordinated P−Se(1) bond is longer, as expected, than the pendant P−Se(2) bond (cf. P−Se, single bond, 2.32 Å)[47] (Table 1). Three C−Ge−C and two C−Ge−Se bond angles {other than C(1)−Ge(1)−Se(1) of 99.31°} lie in the range 109−112°; the geometry around Ge center can be treated as distorted tetrahedral. The structures of **4**, **6**, and **7** are identical to that of **1** and are listed in Supporting Information (S1−S3). The structures of all four compounds are analogous to those of dithiophosphates, $[Ph_3M\{\eta^1\text{-}S(S)P(OR)_2\}]$ (M = Ge,[42] Sn,[43] Pb[40]).

NMR Spectroscopies. The NMR data (^1H, ^{31}P, ^{77}Se) of all of the complexes are listed in the Experimental Section. The ^1H NMR spectral data showed peaks due to CH_3, CH_2, OCH_2, and CH protons of the alkoxyl groups and ring protons of the phenyl groups, usually as multiplets in their characteristic regions. Ph_3M-ring protons showed two sets of signals, a low field due to *o*-protons and a high field due to *m*- and *p*-protons. These phenyl protons are not sensitive to various OR groups or to the nature of metals; however, Pb(IV) was found to show these ring protons at somewhat low field, vis-à-vis those of Ge(IV) or Sn(IV) compounds. The ^{31}P NMR spectrum of compound **1** showed one singlet at δ 70.3 ppm with two pairs of satellites due to $^{31}P-^{77}Se$ coupling, and the occurrence of two pairs is due to the coordinated and pendant Se donor atoms. The coordinated Se atom showed $^1J_{P-Se}$ coupling constant of 527 Hz, while the pendant Se showed $^1J_{P-Se}$ of 876 Hz, and the same trend was shown by compounds **2** and **3**. The ^{77}Se NMR spectrum showed two doublets for each of the compounds **1**−**3**; the substituents affect the chemical shift as expected, and for the coordinated Se, the order of chemical shift to low field varied as ^{i}Pr ≫ ^{n}Pr ≈ Et. There is an irregular trend in pendant Se donor atoms.

Lability of Sn−Se and Pb−Se Bonds. One of the most interesting features of the present investigations is the observation of fluxionality of Sn−Se and Pb−Se bonds at room temperature and the lack of it in the case of the Ge−Se bonds. The ^{31}P NMR of compound **4** at room temperature showed one singlet at δ 70.1 ppm and two pairs of satellites. One pair of satellites is due to $^{31}P-^{77}Se$ coupling ($^1J_{P-Se}$, 695 Hz), and the second pair is due to $^{31}P-^{119}Sn$ coupling ($^2J_{P-Sn}$, 59.1 Hz). As noted for germanium, there were two pairs of satellites due to the coordinated and the pendant Se donor atoms. However, in the case of compound **4**, the appearance of one set of satellites showed the exchange of coordinated Se atom with the pendant Se atom and vice versa (eq 2). From this observation, it is inferred that the Sn−Se bonds are labile at ambient temperature and the NMR spectrometer has recorded the average effect of the two types of Se atoms on coupling with ^{31}P nucleus. When the ^{31}P NMR spectrum of **4** was recorded at −90 °C in CD_2Cl_2, there appeared again two sets of satellites due to the coordinated and pendant Se donor atoms ($^1J_{P-Se}$, 530, 859 Hz), along with a pair of satellites due to $^{31}P-^{119}Sn$ coupling ($^2J_{P-Sn}$, 57.1 Hz).



(2)

The room temperature and variable temperature (VT) NMR spectral characteristics of compounds **5**−**9** are similar to those of **4**; however, in the case of Pb, the ^{31}P signals appear at somewhat lower field as compared to either Ge or Sn compounds. Furthermore, it may be noted that the $^1J_{P-Se}$ values of lead compounds are higher for the coordinated PSe group (**7**, 558 Hz; **8**, 557 Hz; **9**, 557 Hz), and the pendant Se donor atoms have smaller $^1J_{P-Se}$ values (**7**, 846 Hz; **8**, 847 Hz; **9**, 847 Hz) than the corresponding values in Sn or Ge compounds (see Experimental Section). This shows a drift in electron density from the pendant P−Se group to the coordinated P−Se group. The exchange energies for compounds **4**−**9** are calculated from the coalescence temperature[48] and lie in the range of 38−46 kJ mol^{-1} (Table 2). A typical spectrum of VT ^{31}P NMR study can be found in Supporting Information.

To establish whether the exchange pathway shown in the eq 2 is intramolecular or intermolecular, VT ^{31}P NMR of equimolar amounts of **4** and **8** in $CDCl_3$ was measured. That the formation of compounds **5** and **7**

---

[46] *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Huheey, J. E., Keiter, E. A., Keiter, R. L., Eds.; Harper Collins College Publishers: New York, 1993.

[47] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[48] Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; John Wiley & Sons: New York, 1989.

Table 2. Exchange Energy between Coordinated and Pendant Se Atoms ($\Delta G^{\ddagger}$)

compound	T, K	δv	$\Delta G^{\ddagger}$, KJmol^{-1}
$(C_6H_5)_3Sn[\eta^1\text{-}Se(Se)P(OEt)_2]$, **4**	243.15	164.64	45.81
$(C_6H_5)_3Sn[\eta^1\text{-}Se(Se)P(O^iPr)_2]$, **5**	208.15	180.25	38.79
$(C_6H_5)_3Sn[\eta^1\text{-}Se(Se)P(O^nPr)_2]$, **6**	243.15	168.18	45.77
$(C_6H_5)_3Pb[\eta^1\text{-}Se(Se)P(OEt)_2]$, **7**	218.15	143.9	41.15
$(C_6H_5)_3Pb[\eta^1\text{-}Se(Se)P(O^iPr)_2]$, **8**	208.15	145.1	39.16
$(C_6H_5)_3Pb[\eta^1\text{-}Se(Se)P(O^nPr)_2]$, **9**	218.15	145	41.13

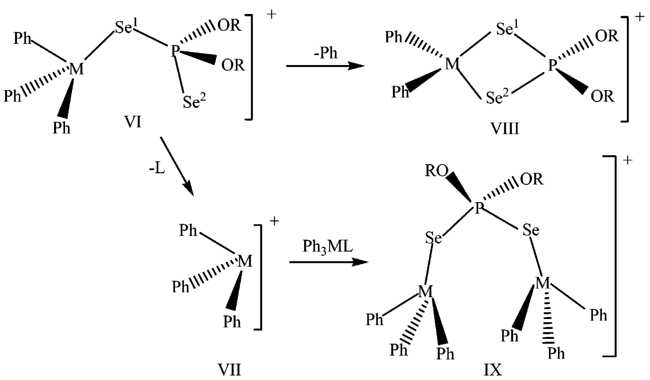
could not be observed in the NMR experiment mentioned above suggests that the exchange is intramolecular and is probably occurring via a four-membered MSe_2P ring. This is in line with the fact that both $^2J(^{31}P-^{119}Sn)$ and $^2J(^{31}P-^{207}Pb)$ do not show much difference with temperature changes and values only marginally decrease. Such data are listed in the Experimental Section for both room temperature and low temperature.

It may be noted that none of compounds (**4**–**9**) displayed ^{77}Se NMR spectra at room temperature, and these results suggest that coalescence has occurred at room temperature. To verify this, a ^{77}Se NMR of a representative compound **4** has been recorded at 40 °C in $CDCl_3$, and it displayed a doublet at $\delta(Se) = 64.2$ ppm with $^1J_{P-Se} = 684.6$ Hz, corresponding to the average of two exchanging Se donor atoms. When the spectra were recorded at low temperature, each of the compounds showed two doublets: one due to the coordinated Se donor atom and a second due to the pendant Se atom like that in germanium.

A look at the δ_{Se} values for the coordinated Se donor atoms for all compounds shows that for each R group, the following trend operates regarding the appearance of signal at low field: Ge > Pb > Sn. This implies that the fluxionality may be due to both the electronic and steric factors. In Sn and Pb compounds, a five-coordinated transition state is easily accessible, whereas in Ge, as a result of smaller atomic size, there is expected more steric repulsion, which appears to prohibit fluxionality. In the related dithiophosphate complexes, such as $R_3Sn\{S(S)P(OEt)_2\}$, the change in line width of ^{119}Sn NMR with temperature was used to study the exchange of coordinated and pendant S donor atoms.[49] Unfortunately, the exchange energy was not available for the comparison between the sulfur and selenium donor atoms.

FAB-Mass Spectrometry. Positive FAB-mass spectra of all the compounds were obtained, and major ions along with their calculated values are listed in the Experimental Section. The matching of calculated isotopic patterns and experimental values confirms the assignment of ions listed. Besides the molecular ion peak, $(Ph_3ML)^+$ (VI), two major peaks that correspond to the intact molecule with the loss of one dsep ligand, $(Ph_3M)^+$ (VII), and one phenyl ring, $(Ph_2ML)^+$ (VIII), respectively, are also detected. Furthermore an additional peak that can be formulated as $[(Ph_3M)_2\{Se_2P(OR)_2\}]^+$ (IX), two triphenylmetal fragments bridged by a dsep ligand, is revealed. A typical fragmentation pattern is listed in Scheme 1. The molecular ion peaks (type VI) are generally weak in intensity, and their intensity varies in the range 1–5%, with the exception of compound **1** for which this value is 10%. The ions with the loss of one phenyl ring (type VIII) are generally strong and exhibit intensity in the range 40–70% for compounds **1**, **4**, **5**, **7**, and **8**, while other compounds show intensity in the range 2–10%. Further, the ions with the loss of one desp ligand (type VII) are normally very strong in intensity (100%) with the exception of compound **9**, for which the intensity was only 5%. Finally, the most significant feature of FAB mass is the observation of the formation of the dinuclear cation bridged by a dsep ligand (type IX), which has shown intensity in the range 4–15% for compounds **1**, **3**–**5**, **7**, and **8**. Compounds **2** and **9** showed only a very weak ion 0.2–1%, and for **6** no peak corresponding to IX was detected. It is worthwhile to mention that the most intense peak for lead compound **9** is detected at $m/z = 514.0$, which corresponds to the molecular ion with the loss of all three phenyl groups.

Scheme 1



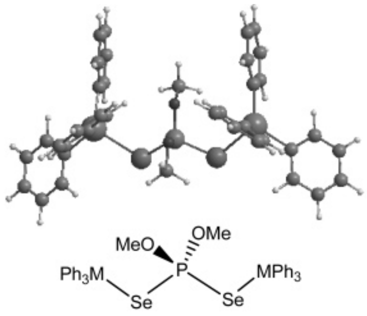
A significant observation is that although compounds **1** and **3** formed nearly equal abundance of molecular ion and dinuclear cation, the same is not true of compounds **4**, **5**, **7**, and **8**, whose dinuclear cations are several times intense over their molecular ions.

Structural Calculations for IX. The FAB-mass spectra showed the formation of the dinuclear cations IX (Scheme 1). Density functional theory calculations are carried out in order to determine the likely structures of these dinuclear cations. The structures predicted for the model dinuclear cations, $[(Ph_3M)_2Se_2P(OMe)_2]^+$ (M = Ge, Sn, Pb), are shown in Figure 2. All three model complexes are isostructural, and the geometry around each of P and M centers are approximately tetrahedral. For comparison, the structures of $[Ph_3M\{\eta^1\text{-}Se(Se)P(OMe)_2\}]$ (M = Ge, Sn, Pb) were also optimized, as shown in Figure 3. The optimized structures are in agreement with the experimental structures of $[Ph_3M\{\eta^1\text{-}Se(Se)P(OEt)_2\}]$ (M = Ge (**1**), Sn (**4**), Pb(**7**)), revealing that the theory used in these calculations is reliable. From the model structures as shown in both Figures 2 and 3, it can be seen that the average P–Se bond distance for a given M is slightly lengthened from $[Ph_3M\{\eta^1\text{-}Se(Se)P(OMe)_2\}]$ to $[(Ph_3M)_2Se_2P(OMe)_2]^+$. The same trend is also observed for the M–Se bonds. Coordination of an additional $[Ph_3M]^+$ to the dsep ligand causes expansion of the coordination sphere around the P atom.

In Scheme 1, it was proposed that the dinuclear cations were formed from reaction of $[Ph_3M]^+$ and $[Ph_3M\{\eta^1\text{-}Se(Se)P(OR)_2\}]$. To study the feasibility of this

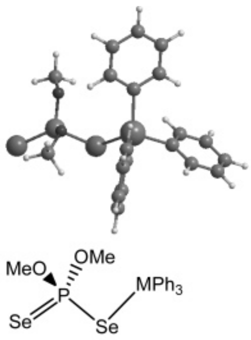
---

[49] Dakternieks, D.; Zhu, H.; Masi, D.; Mealli, C. *Inorg. Chem.* **1992**, *31*, 3606.



	M=Ge	M=Sn	M=Pb
P-O:	1.636	1.638	1.643
P-Se:	2.231	2.225	2.218
M-Se:	2.539	2.717	2.799
M-C:	1.948	2.121	2.176
Se-P-Se:	105.2	107.3	108.2
O-P-O:	95.5	95.2	94.9
M-Se-P:	105.0	102.2	101.6

Figure 2. Calculated structures for $[(Ph_3M)_2Se_2P(OMe)_2]^+$ (M = Ge, Sn, Pb). The bond distances are given in angstroms and the bond angles are given in degrees.



	M=Ge	M=Sn	M=Pb
P=Se:	2.116(2.078)	2.116(2.076)	2.117(2.071)
P-Se	2.292(2.219)	2.288(2.194)	2.279(2.199)
M-Se:	2.456(2.405)	2.621(2.571)	2.689(2.658)
M-C:	1.962(1.941)	2.136(2.132)	2.191(2.191)
Se-P-Se:	111.8(109.6)	113.9(112.7)	113.9(111.1)
M-Se-P:	104.4(105.2)	99.0(101.1)	98.5(101.8)

Figure 3. Calculated structural parameters for $[Ph_3M(\eta^1\text{-}Se(Se)P(OMe)_2]$ together with those observed (in parentheses) experimentally for **1**, **4** and **7**. The bond distances are given in angstroms and the bond angles are given in degrees.

proposal, the energies (ΔE) for the reactions shown in the eq 3 were estimated.

$$[Ph_3M]^+ + [Ph_3M\{\eta^1\text{-}Se(Se)P(OMe)_2\}] \rightarrow [(Ph_3M)_2Se_2P(OMe)_2]^+ \quad (3)$$

We obtained ΔE(Ge) = −37.01 kcal/mol, ΔE(Sn) = −39.03 kcal/mol, and ΔE(Pb) = −36.13 kcal/mol. These results suggest that affinity of $[Ph_3M]^+$ for $[Ph_3M\{\eta^1\text{-}Se(Se)P(OR)_2\}]$ is strong, supporting the proposal given in Scheme 1. The results also reveal that $[Ph_3Sn]^+$ has the strongest affinity for the dsep ligand and $[Ph_3Pb]^+$ the weakest. On the basis of these reaction energies, it is noted that the dinuclear cations are stable and may be isolated if suitable counteranions are used.

In conclusion, the first organometallic derivatives containing dsep ligands in the monodentate connective pattern (η^1-Se) were revealed in the group 14 metals (Ge, Sn, and Pb). The exchange of coordinated and pendant Se atoms for triphenyltin and triphenyllead was explored by the VT ^{31}P NMR, of which the line shapes of satellite pairs provide important data for the calculation of exchange energy, which was not available in their corresponding sulfur analogues. Furthermore, an interesting dinuclear cation, $[(Ph_3M)_2Se_2P(OMe)_2]^+$, identified in the positive FAB mass spectrum, was studied by the density functional theory calculation for its structure and the possible formation pathway. DFT calculations for the molecular complexes were also carried out.

Experimental Section

Materials and Instruments. All chemicals and reagents were purchased from commercial sources and used as received. Commercial ROH were distilled from Mg. Hexane and diethyl ether were distilled from Na/K. All reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting materials, Ph_3MCl (M = Ge, Sn, Pb), were purchased from Aldrich Chemical Co. The ligand, $NH_4Se_2P(OR)_2$ (R = Et, ^{i}Pr, ^{n}Pr), were prepared according to literature methods.[14] The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. ^1H and ^{31}P NMR spectra were recorded on an Advance-300 Fourier transform spectrometers. ^{77}Se NMR spectra at 20 °C were done on a Bruker AC-F200 and at −60 °C were done on Bruker DMX-500 MHz. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra are referenced externally against 85% H_3PO_4 (δ = 0) and PhSeSePh (δ = 463), respectively. Positive FAB mass spectra were carried out on a VG 70-250S mass spectrometer with nitrobenzyl alcohol as the matrix.

X-ray Crystallography. The diffraction data for all complexes was collected at 293 K on a Bruker P4 diffractometer, which was equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. All crystals were mounted on the top of a glass fiber with epoxy cement. The data were collected using 2θ-ω scan technique. Data reduction was performed with SAINT,[50] which corrects for Lorentz and polarization effects. An empirical absorption correction (Ψ scans) was applied. All structures were solved by the use of direct methods, and the refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package,[51] incorporated in SHELXTL/PC V5.10.[52] Selected crystal data for the compounds are summarized in the Experimental Section.

Computational Details. Density functional theory calculations at the B3LYP level[53] were used to optimize all the model complexes. The effective core potentials of Hay and Wadt with double-ζ valance basis sets (LanL2DZ)[54] were chosen to describe P, Se, Ge, Sn, and Pb. The 6-31G basis set was used for C, H, and O atoms.[55] Polarization functions were also added for P (ζ_d = 0.340), Se (ζ_d = 0.338), Ge (ζ_d = 0.246), Sn(ζ_d = 0.183), and Pb(ζ_d = 0.164).[56] All calculations were performed with the Gaussian 03 software package.[57]

$[(C_6H_5)_3Ge\{(\eta^1\text{-}Se(Se)P(OEt)_2)\}]$, 1. Diethyl ether (50 mL) was added to a 1:1 mixture of $(C_6H_5)_3GeCl$ (0.55 g, 1.609 mmol)

---

(50) *SAINT V4.043: Software for the CCD Detector System*; Bruker Analytical X-ray System: Madison, WI, 1995.

(51) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(52) *SHELXL 5.10 (PC Verson): Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray System: Madison, WI, 1998.

(53) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev.* **1988**, *B37*, 785.

(54) (a) Hay, P. J.; Wadt W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(55) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

and NH$_4$Se$_2$P(OEt)$_2$ (0.46 g, 1.548 mmol). The mixture was slowly stirred at 0 °C for 3 h, the solid NH$_4$C1 formed during reaction was filtered, and the filtrate was evaporated slowly under vacuum. The residue obtained was then redissolved in dichloromethane and layered with hexane, which afforded crystalline material of **1**. Yield: 0.82 g, 90%. Anal. Calcd for C$_{22}$H$_{25}$O$_2$PSe$_2$Ge: C 45.33, H 4.32. Found: C 45.76, H 4.57. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.91 (6H, t, CH$_3$), 3.74 (2H, q, CH$_2$), 3.99 (2H, q, CH$_2$); 7.42 (9H, m, *m*- and *p*-Ph); 7.65 (6H, m, *o*-Ph)). ^{31}P{^{1}H} NMR (121.49 MHz, CDCl$_3$, δ, ppm, J, Hz): 70.3 ($^1J_{\mathrm{P-Se},}$ 527, 876). ^{77}Se NMR (38.18 MHz, CDCl$_3$, δ, ppm, J, Hz): 11.4 (d, $^1J_{\mathrm{P-Se},}$ 873), 142.0 (d, $^1J_{\mathrm{P-Se}}$, 530). FAB-Mass, m/z = 305 (303.9) [Ph$_3$Ge$^+$, 100%], 506.9 (505.8)[Ph$_2$GeL$^+$, 40%], 583.9 (582.9) [Ph$_3$GeL$^+$, 10%], 886.9(886.8) [(Ph$_3$Ge)$_2$L$^+$, 9%].

Crystal data for 1: C$_{22}$H$_{25}$GeO$_2$PSe$_2$, $M = 582.9$, triclinic, $P(-)1$, $a = 9.3288(10)$ Å, $b = 10.7266(8)$ Å, $c = 12.8123(10)$ Å, $\alpha = 103.002(6)°$, $\beta = 99.340(7)°$, $\gamma = 99.322(7)°$, $V = 1206.09(18)$ Å^3, $Z = 2$, $D_c = 1.605$ g cm^{-3}, $\mu = 4.368$ mm^{-1}, $T = 293(2)$ K, no. of unique reflections 3111, $R_{\mathrm{int}} = 0.0273$, 2502 reflections with [$I > 2\sigma(I)$], final indices R1 = 0.0407, wR2 = 0.1028.

Compounds **2**–**9** were prepared by a similar method and important data are listed for each compound.

[(C$_6$H$_5$)$_3$Ge{η^1-Se(Se)(O^{i}Pr)$_2$}], 2. Yield: 0.87 g, 86%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Ge: C 47.18, H 4.78. Found: C 48.56, H 4.87. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm); 1.01 (6H, m, CH$_3$), 1.07 (6H, m, CH$_3$), 4.76 (2H, m, CH), 7.44 (9H, m, *m*- and *p*-Ph), 7.67 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CDCl$_3$, δ, ppm, J, Hz): 65.3 ($^1J_{\mathrm{P-Se},}$ 522, 868). ^{77}Se NMR (38.18 MHz, CDCl$_3$ δ, ppm, J, Hz): 1.98 (d, $^1J_{\mathrm{P-Se},}$ 868), 186.3 (d, $^1J_{\mathrm{P-Se}}$, 522). FAB-Mass, m/z = 305(303.9) [Ph$_3$Ge$^+$, 100%], 534 (533.9) [Ph$_2$GeL$^+$, 2%], 611(610.9) [Ph$_3$GeL$^+$, 3%], 915 (914.9) [(Ph$_3$Ge)$_2$L$^+$, 0.2%].

[(C$_6$H$_5$)$_3$Ge{η^1-Se(Se)(O^{n}Pr)$_2$}], 3. Yield: 0.80 g, 85%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Ge: C 47.18, H 4.78. Found: C 47.76, H 5.07. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.75 (6H, m, CH$_3$), 1.37 (4H, m, CH$_2$), 3.76 (4H, m, OCH$_2$), 7.43 (9H, m, *m*- and *p*-Ph), 7.68 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CDCl$_3$, δ, ppm, J, Hz): 71.3 ($^1J_{\mathrm{P-Se},}$ 527, 876). ^{77}Se NMR (38.18 MHz, CDCl$_3$ δ, ppm, J, Hz): 7.1 (d, $^1J_{\mathrm{P-Se},}$ 870), 142.6 (d,^{1} $J_{\mathrm{P-Se}}$, 531). FAB-Mass, m/z = 305.0 (303.9) [Ph$_3$Ge$^+$, 100%], 534.8(533.9) [Ph$_2$GeL$^+$, 10%], 611.8 (611) [Ph$_3$GeL$^+$, 5%], 914.9(914.9) [(Ph$_3$Ge)$_2$L$^+$, 4%].

[(C$_6$H$_5$)$_3$Sn{(η^1-Se(Se)P(OEt)$_2$)}], 4. Yield: 0.92 g, 87%. Anal. Calcd for C$_{22}$H$_{25}$O$_2$PSe$_2$Sn: C 42.01, H 4.01. Found: C 42.23, H 3.84. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm); 0.98 (6H, m, CH$_3$), 3.91 (4H, m, CH$_2$), 7.43 (9H, m, *m*- abd *p*-Ph), 7.67 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at rt, 70.1 ($^1J_{\mathrm{P-Se}}$ 695, $^2J_{\mathrm{P-Sn}}$ 59.1); at −90 °C, 71.6 ($^1J_{\mathrm{P-Se}}$ 530, 859, $^2J_{\mathrm{P-Sn}}$ 57.1); ^{77}Se NMR (95.38 MHz, CD$_2$Cl$_2$ δ, ppm, J, Hz): at −60 °C, 13.2 (d, $^1J_{\mathrm{P-Se}}$ 864), 58.3 (d, $J_{\mathrm{P-Se}}$ 541). FAB-Mass, m/z = 351 (350) [Ph$_3$Sn$^+$, 100%], 552.8(551.9) [Ph$_2$SnL$^+$, 70%], 628.9(629.0) [Ph$_3$SnL$^+$, 3%], 978.8(979.0) [(Ph$_3$Sn)$_2$L$^+$, 10%].

Crystal data for 4: C$_{22}$H$_{25}$O$_2$PSe$_2$Sn, $M = 629.00$, triclinic, $P(-)1$, $a = 9.4980(18)$ Å, $b = 10.2047(16)$ Å, $c = 13.0089$ (19) Å, $\alpha = 97.550$ (12)°, $\beta = 91.667(16)°$, $\gamma = 98.835(13)°$, $V = 1233.6(4)$ Å^3, $Z = 2$, $D_c = 1.693$ g cm^{-3}, $\mu = 4.065$ mm^{-1}, $T = 293(2)$ K, no. of unique reflections, 3174, $R_{\mathrm{int}} = 0.0224$, 2839 reflections with [$I > 2\sigma(I)$], final indices R1 = 0.0325, wR2 = 0.0807.

[(C$_6$H$_5$)$_3$Sn{η^1-Se(Se)(O^{i}Pr)$_2$}], 5. Yield: 1.33 g, 89%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Sn: C 43.87, H 4.45. Found: C 44.42, H 4.51. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.15 (12H, m, CH$_3$), 4.78 (2H, m, CH), 7.43 (9H, m, *m*- and *p*-Ph); 7.73 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at rt, 63.9 ($^1J_{\mathrm{P-Se}}$ 686, $^2J_{\mathrm{P-Sn}}$ 58.4); at −90 °C, 65.1($^1J_{\mathrm{P-Se}}$ 485, 846; $^2J_{\mathrm{P-Sn}}$ 52.0). ^{77}Se NMR (95.38 MHz, CD$_2$Cl$_2$ δ, ppm, ^1J, Hz): At −60 °C, 23.6 (d, $^1J_{\mathrm{P-Se}}$ 854, Se.), 132.8(d, $^1J_{\mathrm{P-Se}}$ 390, Se.). FAB-Mass, m/z = 351(350) [Ph$_3$Sn$^+$, 100%]; 580.9(580.0) [Ph$_2$SnL$^+$, 40%], 657.9(657.1) [Ph$_3$SnL$^+$, 1%], 1006.2(1007.1) [(Ph$_3$Sn)$_2$L$^+$, 6.5%]

[(C$_6$H$_5$)$_3$Sn{η^1-Se(Se)(O^{n}Pr)$_2$}], 6. Yield: 0.77 g, 87%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Sn: C 43.87, H 4.45. Found: C 43.02, H 4.36. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.75 (6H, t, CH$_3$), 1.38 (4H, m, CH$_2$), 3.80 (4H, t, OCH$_2$); 7.43 (9H, m, *m*- and *p*-Ph), 7.68 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at rt, 70.5 ($J_{\mathrm{P-Se}}$ 693, $^2J_{\mathrm{P-Sn}}$ 58.0); at −90 °C, 72.1 ($J_{\mathrm{P-Se}}$ 526, 863; $^2J_{\mathrm{P-Sn},}$ 50.9). ^{77}Se NMR (95.38 MHz, CD$_2$Cl$_2$ δ, ppm, J, Hz): at −60 °C, 19.3 (d, $J_{\mathrm{P-Se},}$ 867), 62.9(d, $J_{\mathrm{P-Se}}$, 515.). FAB-Mass, m/z = 351(350) [Ph$_3$Sn$^+$, 100%]; 580.9 (580.0) [Ph$_2$SnL$^+$, 2%], 657.0(657.1) [Ph$_3$SnL$^+$, 2%].

Crystal data for 6: C$_{24}$H$_{29}$O$_2$PSe$_2$Sn, $M = 657.05$, triclinic, $P(-)1$, $a = 9.5653(15)$ Å, $b = 10.4242(15)$ Å, $c = 13.5634(16)$ Å, $\alpha = 96.147(9)°$, $\beta = 90.109(12)°$, $\gamma = 99.216(12)°$, $V = 1327.0(3)$ Å^3, $Z = 2$, $D_c = 1.644$ g cm^{-3}, $\mu = 3.783$ mm^{-1}, $T = 293(2)$ K, no. of unique reflections, 3446, $R_{\mathrm{int}} = 0.0242$, 3082 reflections with [$I > 2\sigma(I)$], final indices R1 = 0.0365, wR2 = 0.0902.

[(C$_6$H$_5$)$_3$Pb{(η^1-Se(Se)P(OEt)$_2$)}], 7. Yield: 0.79 g, 89%. Anal. Calcd for C$_{22}$H$_{25}$O$_2$PSe$_2$Pb: C 36.83, H 3.51. Found: C 37.47, H 3.87. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, δ, ppm): 0.98 (6H, m, CH$_3$), 3.89 (4H, m, CH$_2$); 7.52 (9H, m, *m*- and *p*-Ph), 7.72 (6H, m, *o*-Ph). ^{31}P{^{1}H} NMR (121.49 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at rt, 73.1 ($^1J_{\mathrm{P-Se}}$ 704, $^2J_{\mathrm{P-Pb}}$ 55.5); at −90 °C, 74.3 ($^1J_{\mathrm{P-Se}}$ 558, 846; $^2J_{\mathrm{P-Pb}}$ 50.2). ^{77}Se NMR (95.38 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at −60 °C, 7.5 (d, $^1J_{\mathrm{P-Se}}$ 857), 99.1 (d, $J_{\mathrm{P-Se}}$ 570.). FAB-Mass, m/z = 439.1 (438.5) [Ph$_3$Pb$^+$, 100%]; 641.0(640.4) [Ph$_2$PbL$^+$, 50%], 717.0 (717.5) [Ph$_3$PbL$^+$, 1%], 1157(1156) [(Ph$_3$Pb)$_2$L$^+$, 15%].

Crystal data for 7: C$_{22}$H$_{25}$PbO$_2$PSe$_2$, $M = 717.50$, triclinic, $P(-)1$, $a = 9.4973(11)$ Å, $b = 10.7536(18)$ Å, $c = 13.0308(18)$ Å, $\alpha = 103.449(11)°$, $\beta = 99.553(7)°$, $\gamma = 99.378$ (11)°, $V = 1247.9(3)$ Å^3, $Z = 2$, $D_c = 1.910$ g cm^{-3}, $\mu = 9.755$ mm^{-1}, $T = 293(2)$ K, no. of unique reflections, 3225, $R_{\mathrm{int}} = 0.0347$, 2826 reflections with [$I > 2\sigma(I)$], final indices R1 = 0.0429, wR2 = 0.1060.

[(C$_6$H$_5$)$_3$Pb{η^1-Se(Se)(O^{i}Pr)$_2$}], 8. Yield: 0.82 g, 82%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Pb: C 38.66, H 3.92. Found: C 39.76, H 4.07. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.11 (12H, m, CH$_3$), 4.76 (2H, m, CH), 7.48 (9H, m, *m*- and *p*-Ph), 7.73 (6H, m, *o*-Ph), ^{31}P{^{1}H} NMR (121.49 MHz, CD$_2$Cl$_2$, δ, ppm, J, Hz): at rt, 67.2 ($J_{\mathrm{P-Se}}$ 695, $^2J_{\mathrm{P-Pb}}$ 61.6); at −90 °C, 68.9 ($J_{\mathrm{P-Se}}$ 557, 847; $^2J_{\mathrm{P-Pb}}$ 52). ^{77}Se NMR (95.38 MHz, CD$_2$Cl$_2$ δ, ppm, J, Hz): at −60 °C, 7.4 (d, $J_{\mathrm{P-Se}}$ 848), 163.7 (d, $^1J_{\mathrm{P-Se}}$ 562). FAB-Mass, m/z = 439.1(438.5) [Ph$_3$Pb$^+$, 100%]; 669.0(668.5) [Ph$_2$PbL$^+$, 40%], 745.0(745.6) [Ph$_3$PbL$^+$, 2%], 1185.1 (1184.1) [(Ph$_3$Pb)$_2$L$^+$, 15%].

[(C$_6$H$_5$)$_3$Pb{η^1-Se(Se)P(O^{n}Pr)$_2$}], 9. Yield: 1.09 g, 85%. Anal. Calcd for C$_{24}$H$_{29}$O$_2$PSe$_2$Pb: C 38.66, H 3.92. Found: C 39.26, H 4.07. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, δ, ppm): 0.73 (6H,

---

(56) Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier Science: Amsterdam, 1984.

(57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B05; Gaussian, Inc.: Pittsburgh, PA, 2003.

m, CH_3), 1.42 (4H, m, CH_2), 3.76 (4H, m, OCH_2), 7.53 (9H, m, *m*- and *p*- Ph), 7.72 (6H, m, *o*-Ph). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, δ, ppm, *J*, Hz): at rt, 73.3 ($^1J_{P-Se}$ 704, $^2J_{P-Pb}$ 58.4); at −90 °C, 74.9($^1J_{P-Se}$ 557, 847; $^2J_{P-Pb}$ 52.2). ^{77}Se NMR(95.38 MHz, CD_2Cl_2, δ, ppm, *J*, Hz): at −60 °C, 11.4 (d, $J_{P-Se,}$ 868), 103.9 (d, $^1J_{P-Se,}$ 551). FAB-Mass, *m/z* = 439.1(438.5) [Ph_3Pb^+, 5%]; 514.0(514.2) [$(M - 3Ph)^+$, 100%], 669.0(668.5) [Ph_2PbL^+, 4%], 743.8(745.6) [Ph_3PbL^+, 0.3%], 1185.1(1184.1) [$(Ph_3Pb)_2L^+$, 1%].

Acknowledgment. We are grateful to the National Science Council of Taiwan (NSC 93-2113-M033-002) for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**, **4**, **6**, and **7** and structures of **4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050291Q